



METHOD USING FLUX SENSORS TO DETERMINE THE OUTPUT OF A  
THERMAL REACTION WITHIN A HOUSING AND DEVICE FOR CARRYING  
OUT SUCH A METHOD

5           The invention is in the field of metrology and more particularly in the field of  
measurements of heat amounts. Its object is a method to estimate the power of a thermal  
reaction inside a housing, such as that of a reactor of a calorimeter. Another of its objects  
is a device for carrying out such a method.

          It is recalled that it is common to estimate and analyze thermal reactions  
10   occurring inside a housing. These thermal reactions are caused, for example, by chemical  
reactions of a reagent, or by the heat produced by biological reactions, such as those  
resulting from the activity of microorganisms, or by physical reactions, such as those  
resulting from crystallization or from the form transition of polymorphic substances, or  
finally by voluntary productions of energy, such as nuclear reactions.

15           More particularly, considering a calorimeter, the housing is placed in a thermally  
controlled environment, so as to maintain a reagent contained inside the housing at a  
desired temperature. This reagent is maintained in an agitated state, through the use of an  
agitation organ or by imparting a movement to the housing itself. The means for  
maintaining at a desired temperature are, for example, obtained by means of an envelope  
20   surrounding the housing for the circulation of a thermostatted heat-exchanging fluid.

          The evolution and analysis of the thermal reaction inside the housing aims more  
particularly at determining its power and the heat exchange coefficient between the wall  
of the housing and the reagent.

A first known technique consists in measuring internal and external temperatures of the housing by means of thermometers. The power of the thermal reaction takes into account the difference between the two measured temperatures, the exchange area and the heat exchange coefficient between the reagent and the wall of the housing.

- 5 According to this technique, the exchange area is estimated approximately and the heat exchange coefficient is determined beforehand through calibration by plunging a heating electric resistance in the reagent. One may refer, for example, to U.S. Patent No. 5,174,655 to Wilfried Litz et al.

- 10 A first drawback of this technique resides in the fact that the exchange area is taken into account arbitrarily by approximate estimation in accordance with the level of the reagent in a quiet state inside the housing. This results in an approximation detrimental to the reliability and exactness of the obtained result regarding the determination of the power of the thermal reaction.

- 15 A second drawback resides in the inadequate use of a means for heating the reagent before its agitation, with, either undesirable consequences on the physical-chemical characteristics of the reagent before the reaction under study, either the preliminary step of determining the coefficient by a specific calibration procedure.

- 20 A second known technique consists in using a heating resistance placed in the heat-transfer fluid circulating between the housing and its envelope. When the reaction under study is exothermic, the heating resistance produces less heat to maintain the reagent temperature constant. The power of the reaction is then estimated from the corresponding power reduction of the heating resistance. One may refer, for example, to U.S. Patent No. 4,130,016 to Lynn C. Walker.

A first major drawback of this technique is that it is not applicable to endothermic reactions.

A second drawback resides in the thermal inertia of the housing against a possible analysis of fast and/or large amplitude thermal variations.

5        A third technique consists in proceeding to a thermal balance in the circulation zone of the heat-transfer fluid. To this effect, for example, a condenser is used in which the heat-transfer fluid condenses after heating. The measurement of the amount of fluid condensed makes it possible to determine the power of the thermal reaction. One may refer, for example, to European Patent EP 0275042 (Westinghouse Electric Corporation).

10       A drawback of this technique resides in the imprecision of the analysis of the thermal reaction inside the housing, estimated through the heat-transfer fluid, which incorporates approximations in measurements, in particular with respect to cumulated thermal losses between the housing and the means used to obtain the thermal balance.

In addition, here also, it results in an approximation detrimental to the reliability  
15 and exactness of the obtained result regarding the determination of the power of the thermal reaction.

The general aim of the present invention is to propose a method to estimate continuously, in real time, in a reliable and precise manner, the power of the thermal reaction inside a housing and the heat exchange coefficient between the reagent and this  
20 housing. Another aim of the invention is to propose a device to carry out this method.

In a general manner, the inventive thought process of the present invention has consisted in proposing a method and its device for carrying it out to determine in a precise and reliable manner, in real time and continuously, the exchange area between the

reagent and the housing, so as to finally make it possible to analyze in the same conditions the characteristics of the housing and of the thermal reaction under study.

This thought process has more particularly consisted in abandoning the habits used in the field, and in using heat flux sensors to determine in a precise, reliable manner,  
5 continuously and in real time, the exchange area between the reagent and the housing.

It results from this thought process that, starting from the use of simple means constituted by heat flux sensors, it is made possible to analyze a thermal reaction, either endothermic or exothermic, and reactions during which the physical-chemical properties of the reagent are likely to evolve rapidly and/or with important amplitudes.

10 In addition, it is made possible to analyze, continuously and in real time, a thermal reaction inside a housing with variations caused voluntarily to the temperature of the reagent, so as to study its evolution.

Thanks to such an unusual exploitation of the heat flux sensors, such as thermopiles providing logical data in tension, it is made possible to obtain reliable  
15 measurements of heat flux through the wall of the housing, which makes it possible to calculate in a precise manner, continuously and in real time, with the use of automated digital computing means, firstly, the level of reagent inside the housing, secondly, the exchange area between the reagent and the wall of the housing, then the thermal power transmitted by the housing, and the heat exchange coefficient between the reagent and the  
20 wall of the housing, and lastly, the power and energy of the thermal reaction.

Another advantageous result of the invention will be noted, which resides in the absence of a preliminary calibration, as in the prior art, for the means used to carry out the method of the invention, i.e., the sensors for measuring the heat flux.

Beyond calorimetry, a need has appeared which resides in the precise and reliable knowledge, continuously and in real time, of the level of a liquid contained in a housing, which may be assimilated to a reagent of the type discussed above as far as its thermal evolution is concerned.

5           Another result attained by the present invention is to propose a method and its device for carrying it out which make it possible to measure, between two given instants  $t_0$  and  $t_1$ , the distance variation, following a thermal reaction, considered between any two points of a reagent contained in the housing at the time  $t_0$  and  $t_1$ .

10           Particular applications of the implementation of the method of the invention consist in particular in measuring the spontaneous variation of the actual level  $h$  of a reagent contained in a housing, in particular a security threshold, following natural variations or variations triggered by the environment outside this housing, such as a storage tank of a delicate product, or also the dilatometry of the material.

15           According to the present invention, it is proposed a method for determining an exchange area  $A$  between a reagent and the wall of a housing containing this reagent, in order to determine in particular the power  $P_r$  of a thermal reaction inside the housing and the heat exchange coefficient  $U$  between the reagent and the housing wall.

20           According to a first aspect of the invention, the method proposed consists in measuring a first heat flux  $F_1$  per surface unit selected in a zone of the wall in secure contact with the reagent, measuring a second heat flux  $F_2$  per surface unit selected in a zone of the wall in secure absence of contact with the reagent, measuring a third heat flux  $F_3$  per surface unit selected in a zone of the wall comprising in a continuous overlapping manner both any zone of the wall in secure contact with the reagent next to any zone of

the wall in secure absence of contact with the reagent, and then calculating the actual level  $h$  of the reagent inside the housing, based on proportions of the measurements of the first, second, and third heat flux which have been carried out.

These dispositions are such that, from the calculated actual level  $h$  of the reagent, and, with respect to any given geometry of the housing, the actual exchange area  $A$  between the reagent and the wall of the housing containing this reagent can be determined, continuously and in real time.

According to another aspect of the method proposed by the invention, the power  $P_t$  transmitted by the housing can be determined by measuring the first heat flux  $F_1$  per surface unit and by determining the said exchange area  $A$  between the reagent and the wall of the housing, preferentially by the method discussed above with respect to a first aspect of the invention.

These dispositions are such that the power  $P_t$  transmitted by the housing can be calculated continuously and in real time, with a precision and a reliability preferentially obtained from those of the exchange area  $A$ , starting from the measurement of the first heat flux  $F_1$  per surface unit, scaled to the totality of the exchange area  $A$  between the reagent  $A$  and the wall of the housing.

Starting from the reliable data collected by the method of the invention, it is next proposed, in a secondary step, to determine the heat exchange coefficient  $U$  between the reagent and the wall of the housing by measuring the temperature  $T_r$  of the reagent and the temperature  $T_e$  of the wall of the housing, by determining the actual exchange area  $A$  between the reagent and the wall of the housing, and by calculating the power  $P_t$  transmitted by the housing.

These dispositions are such that the heat exchange coefficient  $U$  between the reagent and the wall of the housing can be calculated continuously and in real time, with a precision and a reliability obtained from those of the exchange area  $A$ , preferentially determined by the general method of the invention.

5           It will be understood that the heat exchange coefficient  $U$  between the reagent and the wall of the housing is then calculated in a manner known to the person of the art, based on the power  $P_t$  transmitted by the housing, the heat exchange area  $A$  between the reagent and the wall of the housing, and the temperature difference between the temperature of the reagent and the temperature of the wall of the housing.

10           It will be noted, however, that an advantageous result specific to the implementation of the method of the invention resides in the direct determination of the heat exchange coefficient between the reagent and the wall of the housing, without preliminary step likely to disturb the reagent.

          Another result of the dispositions of the invention is a monitoring, continuously  
15   and in real time, of the modifications of the physical-chemical properties of the reagent, such as, for example, an increase in its viscosity during the thermal reaction under study.

          Finally, another result of these dispositions is the possibility of simulating with a great precision thermal reactions in reactors of a larger size.

          Starting from the reliable data collected by the method of the invention, the power  
20    $P_r$  of the reaction is determined by measuring the evolution of the reagent temperature during the time of the reaction, by determining the power  $P_t$  transmitted by the housing, and by estimating the thermal losses of the housing. These thermal losses, commonly

referred to as “heat losses through the reactor head assembly”, are elements known to the person of the art.

These dispositions are such that the power  $P_r$  of the reaction can be calculated, continuously and in real time, with a precision and a reliability obtained from those of the exchange area  $A$ , preferentially determined by the general method of the invention.

It will be understood that the power  $P_r$  of the reaction can be calculated in the manner known to the person of the art, from the mass and the physical-chemical characteristics of the reagent, the evolution of the temperature  $T_r$  of the reagent as a function of time, the power  $P_t$  transmitted by the housing, and the thermal losses of the housing.

It will be understood also that the energy of the reaction is obtained, in the manner known to the person of the art, by integration as a function of time of the power of the reaction measured continuously during the thermal reaction.

According still to the present invention, with respect to a device for carrying out the method proposed in its generality, this device comprises:

- a first housing designed to receive the reagent,
- a first heat flux sensor for measuring the first heat flux  $F_1$  per surface unit, this sensor being arranged at the external wall of the housing in a zone opposed to its internal face, in secure contact with the reagent,
- a second heat flux sensor for measuring the second heat flux  $F_2$  per surface unit, this sensor being arranged at the external wall of the housing in a zone opposed to the internal face, in secure absence of contact with the reagent,



- a third heat flux sensor for measuring the third heat flux  $F_3$  per surface unit, this sensor being arranged at the external wall of the housing in a zone opposed to its internal face, both in presence and in absence of contact with the reagent.

Such a device comprises also advantageously first electronic means for  
5 calculating the level  $h$  of the reagent from logical voltage data provided by the first, second, and third heat flux sensors, and second electronic means for calculating the actual exchange area  $A$  between the reagent and the wall of the housing, from logical data provided by the first electronic means and from the first memory means of the geometric characteristics of the housing, preliminarily captured.

10 According to a particular organization of the device of the invention in calorimetry, this device also comprises a jacket surrounding the housing for the circulation of a fluid around this housing, the fluid being thermostatted by heat-producing means, so as to maintain the housing at a desired temperature.

Still according to this organization, the device of the invention comprises  
15 preferentially a first temperature sensor placed inside the housing to measure the temperature  $T_r$  of the reagent, and a second temperature sensor placed inside the envelope to measure the temperature  $T_e$  of the wall of the housing, obtained in particular from the measurement of the temperature of the heat-transfer fluid inside the envelope, in the manner known to the person of the art.

20 According to a preferred embodiment, the device of the invention comprises additionally third electronic means for calculating the power  $P_t$  transmitted by the housing and fourth electronic means for calculating the heat exchange coefficient  $U$  between the reagent and the wall of the housing, from logical data provided by the second

electronic calculation means, and from the logical data provided by the first and second temperature sensors.

Preferentially also, the device of the invention comprises fifth electronic means for calculating the power  $P_r$  of the thermal reaction from logical data provided by the third electronic calculation means and by the first temperature sensor.

It will also be noted that the first, second, and third heat flux sensors constitute advantageously general means for determining continuously the level  $h$  of a reagent inside the housing, in association with the first calculation means.

It will be noted further that the first, second, third, fourth, and fifth electronic calculation means are advantageously grouped in general memory and electronic calculator means.

It will be noted, finally, that the device of the invention comprises in particular a calculator comprising general memory and electronic calculation means, means for displaying the various measured and calculated logical data, such as screen, printer, or the like, and means for capturing data and controlling general calculation means, such as a keyboard or the like.

The present invention will be better understood and details regarding the invention will be apparent from the description below of a preferred embodiment, made in reference to the only figure of the annexed sheet of drawings, which illustrates schematically an example of embodiment of a device carrying out a general method of the invention.

On the figure, a device proposed by the invention comprises in its generality:

- a calorimeter, comprising a housing 2, a jacket 3 disposed around this housing 2 for the circulation of a fluid 17, and means 18 for producing heat in the fluid 17 to maintain the reagent at a desired temperature,

- heat flux sensors 4,5,6 which equip the housing 2,
- 5 - general memory and electronic calculation means 9.

The above-mentioned flux sensors 4,5,6 are comprised in particular of:

- a first annular sensor 4, placed in contact with and around the external face of the wall of the housing 2, at the base of this housing,
- a second annular sensor 5, placed in contact with and around the external face of  
10 the wall of the housing 2, at the top of this housing,
- a third band-shaped sensor 6, placed in contact with and along a generatrix of the external face of the wall of the housing 2, so as to straddle continuously zones of this housing in correspondence with zones of the internal face of the wall of the housing 2 respectively in contact and in absence of contact with the reagent 1.

15 Further, the housing 2 is equipped with a first temperature sensor 7 measuring the temperature  $T_r$  of the reagent 1 and with a second temperature sensor 8 measuring the temperature  $T_f$  of the fluid contained in the jacket 3, in order to know the temperature  $T_e$  of the wall of the housing.

Each of these heat flux sensors 4,5,6 and temperature sensors 7,8 is connected to  
20 the general electronic calculation means 9.

It will be noted that the housing 2 is equipped in particular with means for agitating the reagent 1, in accordance with known dispositions usual in the field, such as

an agitator 10, and with fixation means 11, 11', 11'' of the flux sensors 4,5,6 on its wall, using, for example, hooks associated to elastic means.

This device makes it possible, advantageously:

- in a first step, to determine, with the first electronic calculation means 12, the  
5 actual level  $h$  of the reagent, from the heat flux  $F_1$ ,  $F_2$ ,  $F_3$  measured respectively by the first, second, and third flux sensors. It will be noted that this determination is obtained from the following formula:

$$F_3 = h \cdot F_1 + (1-h) \cdot F_2$$

- in a second step, to determine, with the second electronic calculation means 13,  
10 the exchange area  $A$  between the reagent 1 and the wall of the housing 2. For a cylindrical housing, such as the one shown on the figure by way of example, this determination is obtained in particular from the following formula:

$$A = a + (2 \cdot \pi \cdot R \cdot c \cdot (F_3 - F_2) / (F_1 - F_2))$$

$a$ : exchange area of the circular base of the housing (in  $m^2$ )

15  $R$ : radius of the cylinder forming the housing (in  $m$ )

$c$ : total height of the vertical flux sensor (in  $m$ )

- in a third step, to determined, with the third electronic calculation means 14, the power  $P_t$  transmitted by the housing 2 from the heat exchange area  $A$  and the flux  $F_1$ . It will be noted that this determination is obtained in particular from the following formula

20 
$$P_t = A \cdot F_1$$

- in a fourth step, to determine , with the fourth electronic calculation means 15, the heat exchange coefficient  $U$  between the reagent 1 and the wall of the housing 2 from the power transmitted by the housing 2, the temperature  $T_r$  of the reagent 1 and the

temperature  $T_e$  of the heat-transfer fluid contained in the envelope 3. It will be noted that this determination is obtained in particular from the following formula:

$$U = P_t / (A \cdot (T_r - T_e))$$

- in a fifth step, to determine, with the fifth electronic calculation means 16, the power  $P_r$  of the thermal reaction under study from the power  $P_t$  transmitted by the housing 2, the evolution of the temperature  $T_r$  of the reagent 1 as a function of time, the mass  $m$  of the reagent, the calorific capacity  $C_p$  of the reagent 1, and the thermal losses of the housing 2. It will be noted that this determination is obtained in particular from the following formula:

$$P_r = P_t + m \cdot C_p \cdot (dT_r / dt) + \text{losses}$$

The energy  $E_r$  of the reaction is thus obtained through integration as a function of time of the power  $P_r$  of the reaction.

It will be noted that the illustrated device comprises additionally a calculator 20 comprising general memory and electronic calculation means 9, display means such as a screen 19, a printer, and data capture and control means 21.

It will be noted also that the general memory and electronic calculation means 9 are organized in the form of software.